THE INFLUENCE OF TEMPERATURE ON STABILITY OF THE STRUCTURE AND PROPERTIES OF METALLIC GLASS

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https://doi.org/10.37904/metal.2019.832

Abstract

This paper presents the results of the effect of temperature on stability of the structure of metallic glass. The iron-based metallic glass was subjected to annealing in the temperature range from 450°C to 650°C during 5 hours. The study found that the increase in the annealing temperature causes an increase in the percentage of the crystalline phase in the amorphous matrix. The examinations included X-ray measurements (phase composition, degree of crystallinity, crystallite sizes), the microscopic observations, and hardness measurement. The X-ray measurements were performed using a Seifert XRD 3003 X-ray diffractometer with the radiation generated by a tube with a cobalt anode.

Keywords: Metallic glass, X-ray phase analysis, X-ray quantitative analysis

1. INTRODUCTION

Continuous and progressing development of modern civilization forces people to make continuous progress in the development of materials used in technology. Materials commonly known as steels or non-ferrous metal alloys are constantly being developed by modification of their composition and structure [1-3]. However, in order to meet the contemporary requirements of the aerospace, automotive, military and energy industries, other groups of materials such as polymers, ceramics and commonly used composites started to be intensively researched and developed [4-6]. An additional group of materials with interesting properties are metal alloys with amorphous structure called metallic glasses. At present, these materials are produced in two forms: thin tapes or solid metallic glasses [7-15]. These materials have a number of unique properties such as high tensile strength, high hardness, high corrosion resistance and very good magnetic properties unavailable for conventional materials with a crystalline structure. One of the problems in using these materials may be their metastable structure, which can change depending on the temperature during operation, thus leading to changes in properties.

2. MATERIAL AND METHODS

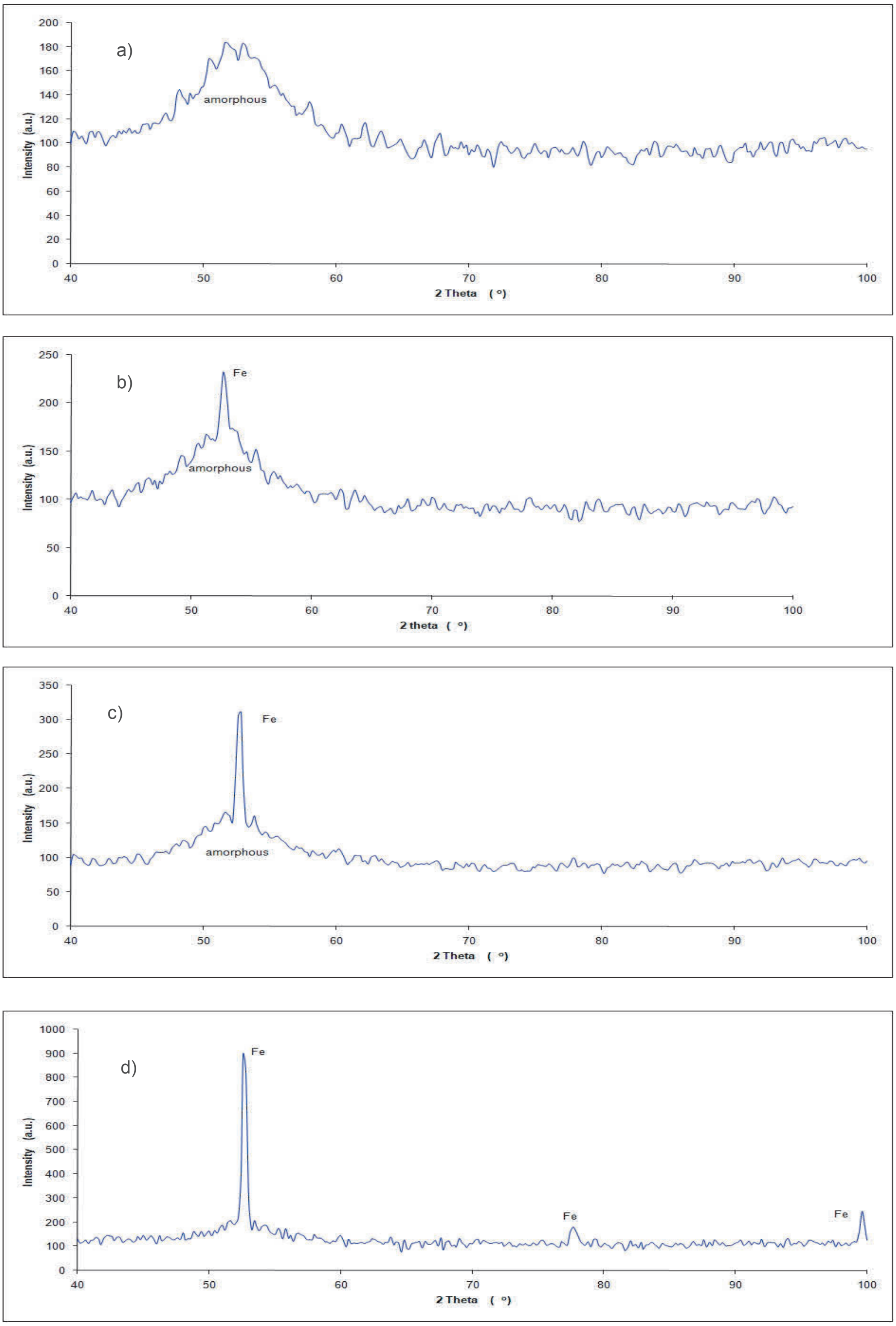
The examinations were performed using an alloy with chemical composition of $Fe_{75}B_{10}Si_7C_8$, which was obtained by rapid cooling of tapes with length of 80 mm, width of 30 mm and thickness of 45 μm. The samples of metallic glass were annealed at temperatures from 450 to 650 °C for 5 hours. The samples obtained after annealing were subjected to X-ray examinations using a SEIFERT X-ray diffractometer with a cobalt anode tube generating radiation. The examinations allowed for:

- Conducting an X-ray phase analysis
- Conducting an X-ray quantitative analysis
- Evaluation of the average size of crystallites

Furthermore, hardness measurement using the Vickers method and microscopic observations using the TEM transmission electron microscope were also conducted to determine the effect of temperature on the properties and structure of the material.

3. RESULTS AND DISCUSSION

The samples obtained after thermal treatment were subjected to X-ray phase analysis, which allowed for determination whether the samples had an amorphous, crystalline or mixed amorphous-crystalline structure. Furthermore, the DHN-PDS X-ray database was used to identify the obtained crystalline phases. Obtained X-ray patterns are presented in **Figure 1**.



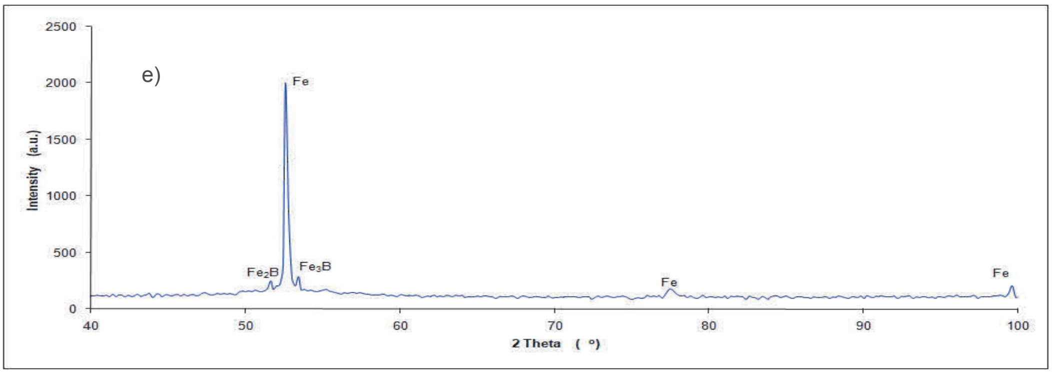


Figure 1 X-ray diffraction of samples annealed at: a) 450 °C, b) 500 °C, c) 550 °C, d) 650 °C, e) 650 °C

The X-ray phase analysis showed that the annealing of metallic glass at 450 °C does not lead to any structural changes compared to the alloy in its initial state. This is evidenced by one broad diffraction reflection characteristic of materials with the amorphous structure as shown in **Figure 1a**. The increase in the annealing temperature initiated crystallization processes. X-ray patterns showed the disappearance of reflections from amorphous phase and the appearance of diffraction reflections from crystal phase. It was found that the reflections obtained came from iron **(Figures 1b, c, d**). Annealing at the temperature of 650°C caused virtually complete disappearance of the amorphous phase and a further increase in the degree of crystallization. X-ray diffraction revealed that apart from Fe crystallites, the boronic phases Fe_2B and Fe_3B also started to form **(Figure 1e**). In order to estimate the fractions of amorphous phase and crystalline phases and the average size of crystallites formed on the obtained X-ray patters, the background was cut off and then the diffraction reflections from the amorphous and crystalline phases were separated. The mathematical Pseudo-Voigt function was used to separate the reflections. An example of deconvolution of diffraction reflections in Analysis software for a sample annealed at 500 °C is shown in **Figure 2**. Assuming that the X-ray intensity in crystalline areas is proportional to the mass fraction of crystalline phases, while the dispersed radiation intensity is proportional to the mass fraction of amorphous phase, the degree of crystallinity can be determined by applying the equation (1), whereas the average size of crystallites formed is obtained from the equation proposed by Scherrer (2) [16].

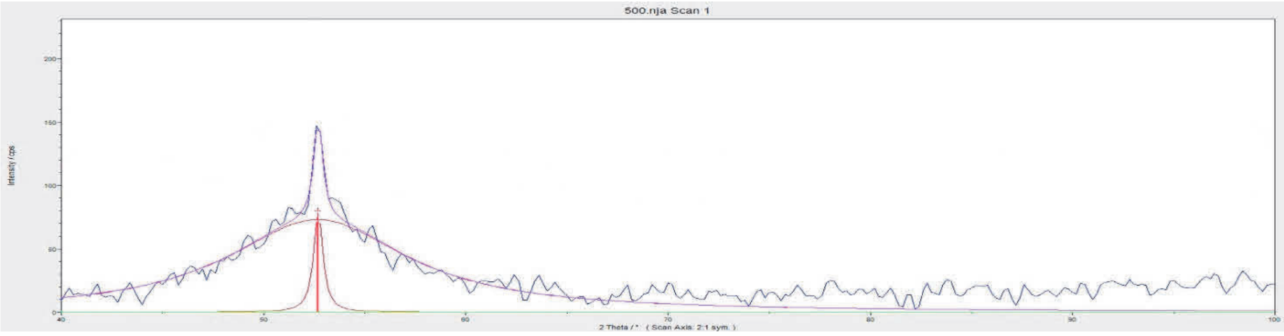


Figure 2 X-ray diffraction of a sample annealed at 500 °C after deconvolution of diffraction reflections by means of the pseudo-Voigt function

$$Sk = \frac{\sum I_{crystalline}}{K * I_{amorphous} + \sum I_{crystalline}} \qquad (1)$$

where: *Sk* represents crystallinity degree (%), $I_{crystalline}$ is intensity of reflections from crystalline phases, $I_{amorphous}$ is intensity of reflections from amorphous phase and *K* is constant.

$$d = \frac{k * \lambda}{\beta * \cos\theta} \tag{2}$$

where: *d* represents size of crystallites (nm), k Scherrer constant, *λ is* wave length of X-radiation used (nm), *β* half width of diffraction reflection and *θ* is Bragg's angle. The obtained results are compared in **Table 1**.

Table 1 Results of measurements of degree of crystallinity, size of crystallites and hardness.

Annealing temperature (°C)	Sk (%)	d (nm)	structure	HV 0.05
Initial state	0	0	amorphous	780 ± 6
450	0	0	amorphous	835 ±9
500	≈ 52	≈ 12	amorphous + Fe	891 ± 4
550	≈ 78	≈ 29	amorphous + Fe	953 ± 6
600	≈ 93	≈ 33	amorphous + Fe	1015 ± 7
650	≈ 99	≈ 37	amorphous + Fe + Fe_3B + Fe_2B	1026 ± 8

In order to evaluate the effect of annealing on mechanical properties, hardness measurements were conducted, with the results shown in **Table 1**, while examples of microstructures are presented in **Figure 3**.

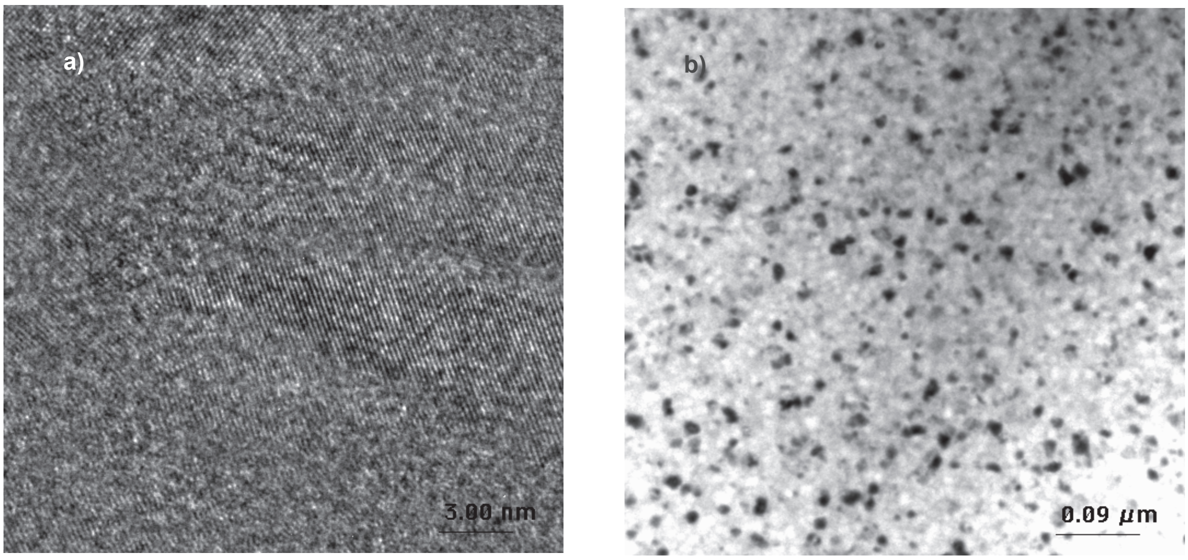


Figure 3 Microstructure of an amorphous sample (a) and a sample annealed at 550 °C (b)

According to the results presented in **Table 1** and **Figure 3**, annealing at temperatures over 450°C causes gradual disappearance of metastable amorphous phase and initiation of crystallization. Firstly, Fe crystallites are formed and they increase their mean size as the annealing temperature rises. Annealing at temperatures above 600 °C leads to almost complete crystallization, whereas in the last stage, the crystallites of boronic phases Fe_3B and Fe_2B begin to form. The examinations presented in the study lead to the conclusion that that during annealing at temperatures over 550 °C, the nucleation rate is the preferred parameter to crystallite growth rate. This is evidenced by significant differences in the degree of crystallinity and small changes in the average size of crystallites obtained. Crystallization processes cause an increase in the hardness of the samples with an increase in the fraction of the crystalline phase. However, plastic properties were reduced compared to the alloy in initial state.

4. CONCLUSION

The examinations conducted in the study lead to the following conclusions:

- Annealing of metallic glass above a certain critical temperature causes structural changes consisting in the initiation of crystallization processes,
- The crystallites formed increase their average size as the annealing temperature rises and the degree of crystallization increases,
- An increase in the fraction of crystalline phase leads to an increase in material hardness.

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